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Title: Multidisciplinary Approaches to Radiation Balanced Lasers (MARBLE):  
1st Annual Progress Report

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## **Progress Report from Efforts Performed at**

*New Mexico Consortium (NMC) and Los Alamos National Laboratory (LANL)*

**Co-PI:** *Markus P. Hehlen, Engineered Materials (NMC, LANL)*

### **I. Summary**

The initial main modifications of the existing  $\mu$ PD crystal-growth system at LANL have been completed. This now gives us the new capability to develop the growth of crystalline RBL materials by both the  $\mu$ PD and the Bridgman method. Quantitative mass spectrometry of the growth atmosphere was conducted to identify possible sources of gaseous trace species (primarily hydrogen) that could cause the undesired reduction of  $\text{Yb}^{3+}$  to  $\text{Yb}^{2+}$  during the crystal growth. Hydrogen was found to be at sufficiently low levels to not be a respective concern. Studies on the thermal decomposition of  $\text{YbF}_3$  to form  $\text{Yb}^{2+}$  are currently underway in collaboration with MARBLE team member Prof. Pauzauskie. First samples of  $\text{Yb}^{3+}$ -doped  $\text{YLiF}_4$  (YLF:Yb) and undoped  $\text{LiLuF}_4$  (LLF) were grown, and MARBLE team member Prof. Sheik-Bahae has performed measurements of laser-induced heating (YLF:Yb) and background absorption coefficient (LLF). We discovered that one or several of the  $\text{YF}_3$ ,  $\text{LiF}$ , and  $\text{YbF}_3$  precursors contains organic impurities that chemically reduce to black residue during the high-temperature growth in oxygen-free argon atmosphere. A process for removal of these residues prior to growth is being considered. Comparing the results from incongruently melting YLF with those of congruently melting LLF indicate that a congruently melting material is preferred for Bridgman growth. Crystal-growth experiments with LLF are currently underway. The results of these studies on  $\text{Yb}^{3+}$  doped materials will be directly applicable to the future growth of  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$  doped as well as  $\text{Yb}^{3+}$ ,  $\text{Nd}^{3+}$  co-doped RBL crystals. There was no activity on the parallel effort of developing rare-earth-doped chalcogenide glasses. The primary reason was a lack of manpower due to a delayed hiring of a student. In September 2017, we have hired a Postdoctoral Researcher who will be able to contribute to the growth (at LANL) and optical characterization (at UNM) of RBL materials.

### **II. Proposed Activity**

#### **a. Grow YLF:Tm and YLF:Er on $\mu$ PD system**

To date, rare-earth-doped fluoride crystals used for solid-state optical refrigeration have been grown exclusively by using the well-established Czochralski method. In this process, the material (*e.g.*  $\text{Yb}^{3+}$ -doped  $\text{YLiF}_4$ ; YLF:Yb) is melted in a crucible, a seed crystal is brought in contact with the melt surface, and a single crystal is then grown by rotating and translating the seed upwards. AC Materials Inc. (Tarpon Springs, FL) has been our primary vendor, and they have been able to grow large (typically 80 g) single crystals of often high purity using this method. The major drawback of this approach is the need for large (typically ~250 g) batches of starting material. Transition-metal impurity levels of <0.1 ppm are needed in order to obtain high-performance materials for laser cooling or RBL. However, it is extremely challenging to reliably achieve such high purities at these large quantities of starting material. As a result, the variation of the external

quantum efficiency and background absorption coefficient from batch to batch and sometimes even within one boule remains one of the major obstacles to advancing solid-state laser cooling and RBL. One goal of the present project, therefore, is the development of a crystal-growth process that operates at a much smaller scale of a few grams where it is more practical to achieve these exceedingly high purities. This would greatly facilitate the development of material purification methods and pave the way for the reliable preparation of high-performance crystals for laser cooling and RBL. We have proposed to demonstrate such a process and grow YLF:Tm and YLF:Er on the existing micro-pulling-down ( $\mu$ PD) crystal-growth system at LANL.

**b. Fabricate & characterize doped chalcogenide glasses / Procure load frame**

As a parallel effort to the growth of crystalline RBL material, we have proposed to explore glassy RBL materials that can be drawn into optical fibers and ultimately be fabricated into micro-structured fibers that can achieve uniform transverse temperature profiles. The focus will be on chalcogenide glasses (sulfides, selenides) as a novel alternative to rare-earth-doped ZBLAN glass. The respective proposed year 1 activities were to fabricate and characterize several candidate glasses as well as to procure a load frame for the extrusion of fiber preforms.

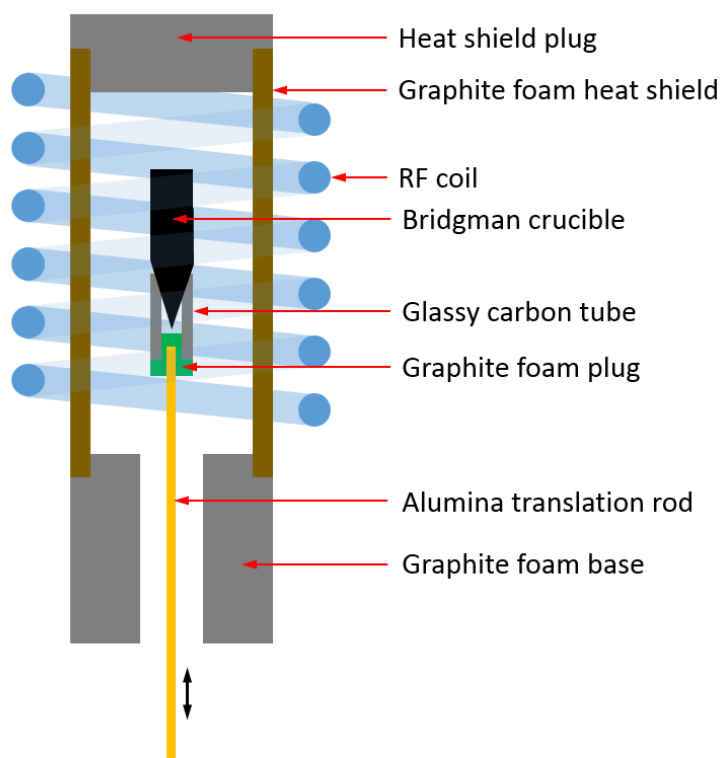
**III. Results, Data and Analysis**

**a. Experiments**

**i. Choice of Crystal-Growth Method**

We are evaluating two potential methods for the growth of high-purity rare-earth-doped fluoride crystals on the few gram scale. The first method is micro-pulling-down ( $\mu$ PD) crystal growth in which a crystal rod is grown downwards from an orifice in the bottom of a crucible. Previously, this method has been used successfully to grow fibers of doped  $\text{LuLiF}_4$  (LLF) by our collaborator Prof. Mauro Tonelli at the University of Pisa. The resulting crystal rods are typically 1.5–2 mm in diameter and sometimes 40–80 mm in length, and they have shown laser action in the case of LLF:Ho. While crystals can be grown from as little as 1 g of starting material,  $\mu$ PD crystal growth can be tricky because of the need to continually adjust the melt viscosity via the melt temperature during the crystal growth in order to offset the decreasing gravitational force of the melt in the crucible while not dropping all of the melt through the orifice. This delicate balance is different for different melts and has to be found by laborious experimentation. The fiber-like shape of the crystals can be suited for RBL, however it does not lend itself to laser-cooling applications in which smaller surface-to-volume ratios are required. In our previous  $\mu$ PD growth of  $\text{LiSrAlF}_6$  (LiSAF), we have also observed evaporative losses (most likely loss of LiF) from the surface of the fibers during growth, which results in rough and often opaque sample surfaces.

The second method is Bridgman crystal growth in which the melt contained in a crucible is slowly crystallized from the bottom up by translating the crucible downward (typically 1 mm/hr) in a static temperature gradient (typically 2–5 K/mm). The Bridgman method has been used by others to grow fluoride single crystals. Compared to  $\mu$ PD crystal growth, the Bridgman method is less challenging to implement and operate, which facilitates the screening of extended compositional and process parameter spaces. Furthermore, the Bridgman method gives access to bulk crystals on the several  $\text{cm}^3$  scale that can be suited for both laser cooling and RBL applications. For these reasons we have chosen to pursue crystal growth of RBL materials using the Bridgman technique in a first campaign.

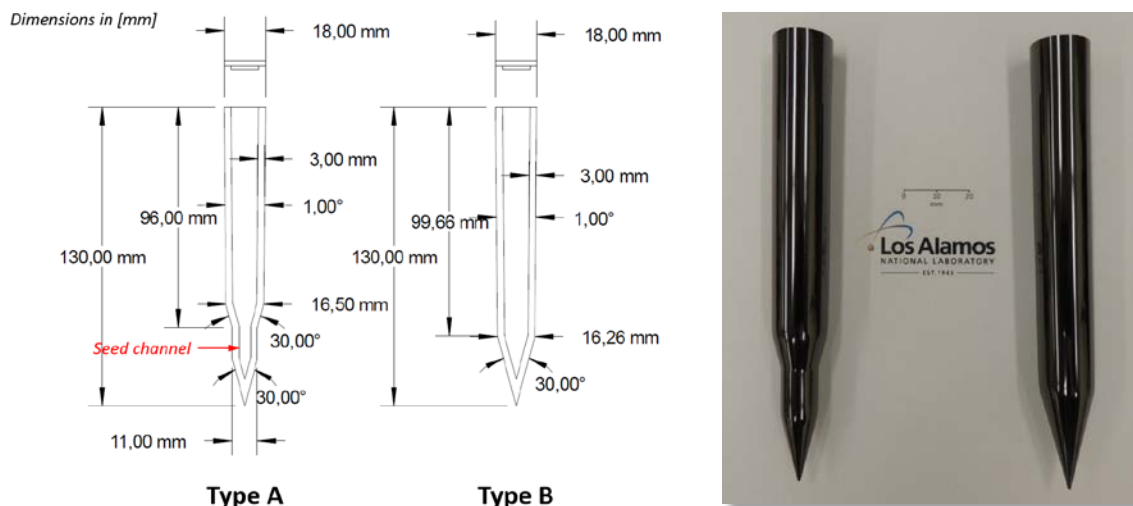


**Figure 1:** Left: Image of the fluoride crystal-growth system at LANL. The growth chamber sits atop a high precision translation stage. The RF generator is seen on the left and the vacuum system is attached on the right of the growth chamber. Right: Cross-sectional representation of the growth section.

#### **i. Reconfiguration of Existing Crystal-Growth System**

We have an existing fully operational  $\mu$ PD fluoride crystal-growth system (Figure 1) at LANL that was developed in collaboration with Prof. Mauro Tonelli (University of Pisa, Italy) as part of a recent previous effort in which we have grown single-crystal fibers of LiSAF. The system includes a computer-controlled radio-frequency (RF) coil that provides heating (to up to 1000 °C) of a

crucible / melt located inside a graphite foam heat shield as well as a high-precision translation stage that allows for the vertical translation of the seed crystal (for  $\mu$ PD) or of a crucible (for Bridgman) with minimal vibrations. The grow chamber and translation stage are designed to operate in high vacuum ( $\sim 10^{-6}$  Torr) or in inert atmosphere (even at pressures exceeding ambient pressure).



**Figure 2:** Left: Cross-sectional drawings of the two types of glassy carbon Bridgman crucibles procured from HTW. Right: Pictures of the procured crucibles.

In a first step in the current project, we have designed and implemented several changes to this  $\mu$ PD system in order to make it suitable for growing crystals by the Bridgman technique. The resulting dual-use system will offer the needed versatility for exploring a wide range of RBL materials. We have performed the following changes:

**New Bridgman crucibles:** While Czochralski and  $\mu$ PD growths typically start from crystallographically oriented single-crystal seeds of the desired material, the Bridgman growth is a self-seeded method. This is achieved by choosing a suited internal crucible shape. Specifically, the bottom of the crucible, which also corresponds to the location of lowest temperature, is shaped as a sharp tip where a small crystal seed first forms spontaneously. This seed then grows as a single crystal as the crucible is slowly lowered in the fixed temperature gradient. Fluoride melts must be contained in oxygen-free crucibles to prevent chemical reactions between the melt and the crucible. Glassy carbon or platinum are common choices. Glassy carbon is not wetted by fluoride melts and can be obtained commercially in intricate internal shapes, while platinum is wetted by fluoride melts and is more difficult to machine in the desired shapes on the inside. We have procured two types of glassy carbon Bridgman crucibles (5 each) from HTW (Thierhaupten, Germany) for the first growths. Cross sectional views of the two crucible types are shown in Figure 2 (left). Type A has a seed channel for the purpose of selecting and growing a high quality crystal

seed before expanding it to a larger diameter in the upper section of the crucible. Type B does not have this seed channel and directly expands the crystal shape to the full diameter at a 30° angle. The upper cylindrical section of both crucibles is slightly conical so that the crystal can be extracted more easily after the growth. Figure 2 (right) shows pictures of both procured crucibles.



**Figure 3:** Existing graphite foam base (left) and new graphite foam base (right).



**Figure 4:** Left: Image individually showing (from the bottom up) the alumina translation rod (white), graphite foam plug, glassy carbon adapter tube, and Type B crucible. Right: Image of the assembled parts.

*New graphite foam bases:* The graphite heat shield inside the RF coil is supported by a graphite foam base (Figure 1, right) which has a center hole to accommodate the translation rod (Figure 3). The 12-mm diameter of the existing  $\mu$ PD graphite foam base was too small for translating an 18-mm diameter Bridgman crucible through it as the crucible translates downward from the heated zone. We therefore designed a new graphite foam base with larger inside diameter and had it fabricated from FPA10 graphite foam by Graftech Advanced Graphite Materials (Parma, OH).

*New graphite adapter:* The  $\mu$ PD setup uses a 2-mm diameter alumina rod (attached to the stepper-motor-driven translation stage below) to translate the growing crystal fiber. We therefore had to design and fabricate a graphite adapter that is suited to support the Bridgman crucible on top of the existing alumina rod. The adapter consists of a graphite plug and a glassy carbon tube (Figure 1, right) on top of which the Bridgman crucible (Figure 4) is placed.

## **ii. Reduction of $\text{Yb}^{3+}$ to $\text{Yb}^{2+}$**

While the 3+ oxidation state is by far the most common one for the rare earths, some ions such as Eu and Yb can also form stable compounds in the 2+ state. In case of Yb-doped materials for solid-state laser cooling or RBL this can be a problem because  $\text{Yb}^{2+}$  has intense (parity allowed) absorption transitions in the visible spectral region. Depending on the crystal host, the long-wavelength tail of these absorption bands could extend into the 1  $\mu\text{m}$  spectral range and cause background absorption of, and thus heating by, the laser light used to pump the RBL. Figure 5 shows an extreme example of a Yb-doped  $\text{BaY}_2\text{F}_8$  (BYF:Yb) crystal (prepared previously at the University of Pisa) in which some of the  $\text{Yb}^{3+}$  had reduced to  $\text{Yb}^{2+}$  during the growth.  $\text{Yb}^{3+}$  has spectrally narrow absorptions around 1  $\mu\text{m}$  and appears colorless; it is the  $\text{Yb}^{2+}$  absorptions in the blue/green spectral range that cause the deep red color of this sample.



**Figure 5:**  $\text{Yb}^{2+}$  contamination in a BYF:Yb crystal (picture taken from Ph.D. dissertation by A. Volpi, 2017, University of Pisa, Italy).

The cause of  $\text{Yb}^{2+}$  formation is relevant to the present effort and is also an ongoing topic of research by our collaborators at the University of Pisa. Reduction of  $\text{Yb}^{3+}$  by reducing agents

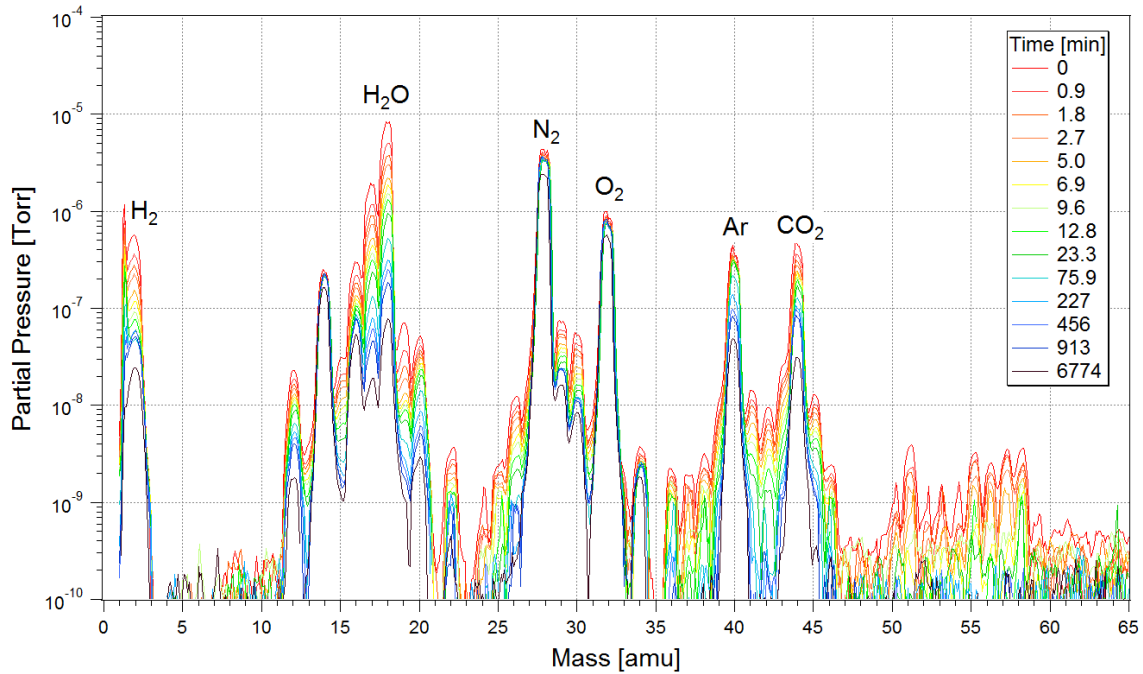


such as trace amounts of hydrogen gas ( $\text{YbF}_3 + \frac{1}{2} \text{H}_2 \rightarrow \text{YbF}_2 + \text{HF}$ ) during the growth has been the leading hypothesis. Over the past few years, the University of Pisa has adopted a process in which 10%  $\text{CF}_4$  is mixed into the argon growth atmosphere. At the crystal-growth temperature, the  $\text{CF}_4$  thermally decomposes to form fluorine gas which can convert (oxidize)  $\text{Yb}^{2+}$  back to  $\text{Yb}^{3+}$ . However, fluorine is very corrosive to the metal furnace components, producing residues that can potentially cause contamination of the crystal by iron. In contrast, we recently learned that AC Materials Inc. grows their high-performance Yb-doped fluoride crystals in nitrogen inert atmosphere without adding reactive agents, lending evidence that trace amounts of reducing gases may not be responsible for  $\text{Yb}^{3+}$  reduction. These observations are further supported by our own growth of YLF:Yb in ultra-high purity grade argon (see Section III.A.iv) that produced a colorless sample without visible signs of  $\text{Yb}^{2+}$ .

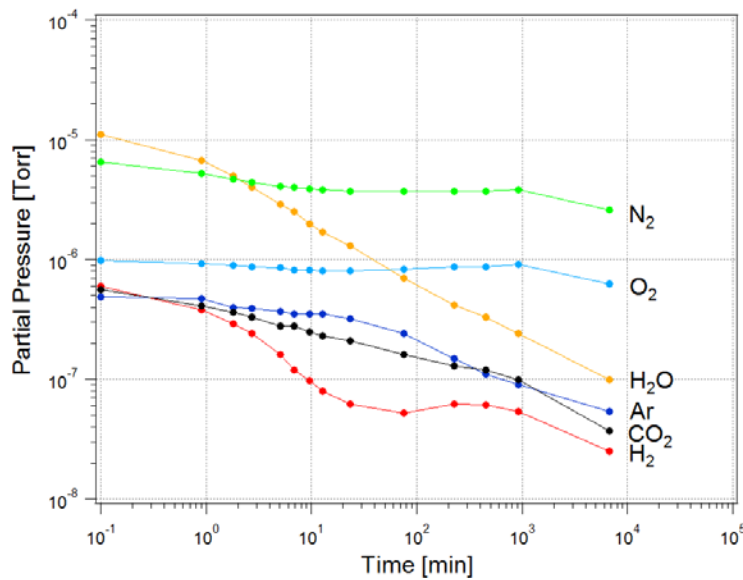
A growth typically begins by establishing a high vacuum in the growth chamber followed by refilling with a known grade of inert / reactive gas. Different gases are pumped at different rates by the turbo pump, and there is a possibility that reducing gases such as hydrogen remain present in significant quantities when the chamber is refilled and subsequently used for the crystal growth. We have therefore installed a residual gas analyzer (RGA) on our growth chamber in order to gather quantitative data on the gaseous composition of the vacuum atmosphere before refilling with inert gas. Figure 6 shows a series of mass spectra recorded by the RGA during turbo pumping of the crystal-growth vacuum chamber. Note that the first spectrum (time=0) was recorded when the total pressure had reached  $\sim 2 \times 10^{-5}$  Torr at which it was safe to operate the RGA. The primary species are  $\text{N}_2$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}$ , Ar,  $\text{CO}_2$ , and  $\text{H}_2$ . Figure 7 shows the corresponding analysis of the individual partial pressures as a function of time. After 18 hours of pumping, the main residual species are  $\text{N}_2$  and  $\text{O}_2$ , making up 70% of the residual gas and both showing relatively slow pumping rates. Water is removed at the highest rate among this set of gases. After 18 hours of pumping, hydrogen is in the mid- $10^{-8}$  Torr range which, at the given temperature and volume inside the crucible, corresponds to  $\sim 4 \times 10^9$   $\text{H}_2$  molecules. In comparison, a 5-g batch of YLF:10%Yb contains  $1.6 \times 10^{21}$   $\text{Yb}^{3+}$  ions. Therefore, if a YLF:Yb batch was grown in this high-vacuum atmosphere and all hydrogen available in the crucible reacted with  $\text{Yb}^{3+}$ , only 1 in  $\sim 10^{11}$   $\text{Yb}^{3+}$  would be converted to  $\text{Yb}^{2+}$ , which is negligible. Refilling the chamber to ambient pressure with Airgas Research Grade argon (certified  $< 0.04$  ppm  $\text{H}_2$ ), which we have procured, would increase the hydrogen concentration by  $500\times$  from the measured high-vacuum condition and thus increase the  $\text{Yb}^{2+}$  fraction to 1 in  $10^{14}$ , assuming all available  $\text{H}_2$  reacted with  $\text{Yb}^{3+}$ . This is still exceedingly low and leads us to reject the hypothesis that residual reducing gases are the cause for  $\text{Yb}^{2+}$  formation, at least in the LANL system.

An alternative hypothesis for the reduction of  $\text{Yb}^{3+}$  is the thermal decomposition of  $\text{YbF}_3$  according to  $\text{YbF}_3 \rightarrow \text{YbF}_2 + \frac{1}{2} \text{F}_2$ . The rate of this reaction is expected to increase with increasing temperature. It should therefore be more pronounced when growing BYF:Yb (melting point  $\sim 995$  °C) compared to growing YLF:Yb (melting point  $\sim 840$  °C) or LLF (melting point  $\sim 810$  °C). This could explain the high  $\text{Yb}^{2+}$  concentration in the BYF:Yb sample shown in Figure 5 and the visual absence of  $\text{Yb}^{2+}$  in YLF:Yb samples grown under a similar argon atmosphere. Nevertheless, a measureable amount of  $\text{Yb}^{2+}$  could be present in our YLF:Yb samples. We are therefore working

with our MURI collaborator Prof. Peter Pauzauskie (University of Washington) who is currently using EXAFS measurements to determine the  $\text{Yb}^{2+}/\text{Yb}^{3+}$  ratio in a  $\text{YLF}:\text{Yb}$  sample grown on our system (see Section III.A.iv).



**Figure 6:** Residual gas mass spectrum at different times during turbo pumping of the crystal growth vacuum chamber.

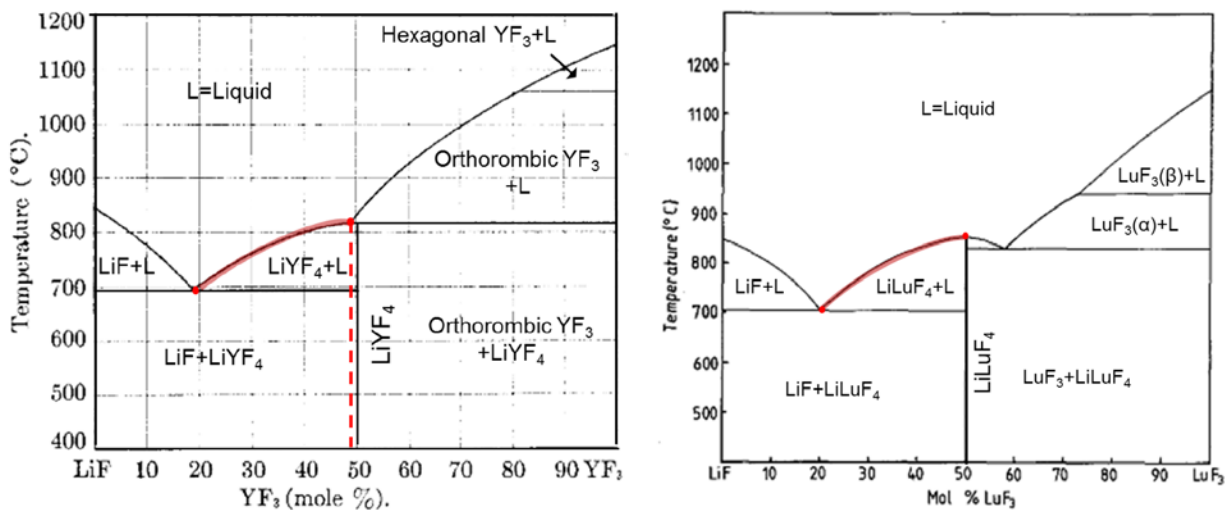


**Figure 7:** Partial pressure of several gases during turbo pumping of the crystal growth vacuum chamber.

### iii. Growth and Characterization of YLF:Yb

Rather than growing the new materials YLF:Tm and YLF:Er, we have chosen to grow the most studied laser-cooling crystal YLF:10%Yb as the first material. Our MURI collaborator Prof. Sheik-Bahae has extensive existing optical characterization capabilities as well as a large number of experimental data on this material, making it possible to quantitatively benchmark our sample. Once developed for YLF:Yb, the Bridgman crystal growth process should be readily applicable to the growth of YLF crystals doped or co-doped with other rare earths.

The preparation of YLF:Yb is a two-step process. In a first step, the polycrystalline starting materials  $\text{YF}_3$ , LiF, and  $\text{YbF}_3$  were mixed and mortared in our argon glovebox. These starting materials were previously obtained from AC Materials Inc. who synthesized  $\text{YF}_3$  and  $\text{YbF}_3$  in house and obtained LiF from GFI Chemicals (optical grade). The stoichiometry of the starting materials is determined by the phase diagram (see Figure 8, left). YLF melts incongruently, *i.e.* the composition of the YLF crystal is different than the melt it grows from. It is therefore necessary to enrich the starting composition with LiF, and we have chosen a ratio of  $\text{LiF}:\text{Y}(\text{Yb})\text{F}_3=0.525:0.475$  (dashed line in Figure 8, left) based on previous experience by our University of Pisa collaborators. As the YLF crystal grows, the composition of the liquid melt will gradually increase in LiF (following the solid red line in Figure 8, left) until the remaining melt freezes at the eutectic point (20%  $\text{YF}_3$  : 80% LiF); *i.e.* it is not possible to obtain 100% yield for the YLF crystal growth.



**Figure 8:** Left: Phase diagram of YLF (taken from Ph.D. dissertation by A. Volpi, 2017, University of Pisa, Italy and R. E. Thoma et al, *J. Phys. Chem.*, 65 (1961) 1096). Right: Phase diagram of LLF (taken from I. R. Harris et al, *J. Mater. Sci.*, 18 (1983) 1235).

The starting materials were then melted in a Type B Bridgman crucible (Figure 9, left) in the box furnace inside the glovebox. While this melting step could have been performed directly

in the crystal-growth system, melting in the glovebox allows us to check the shape of the reacted material inside the crucible, and it offers the future possibility of performing electrochemical purification of the melt. The result of the YLF:Yb melting step was polycrystalline and opaque sample that (1) had a significant amount of black residue on its surface and (2) had a dull tip rather than the sharp tip given by the crucible. The black residue could be removed by wiping the surface of the sample. The dull tip is a potential problem as it may prevent the formation of a single well-defined seed in the subsequent growth. Its formation is likely a result of the fluoride melt not wetting the glassy carbon crucible surface and thus not completely flowing into the crucible tip.

In a second step, this sample was installed in the crystal-growth system. A high vacuum was established in the chamber (Figures 6 and 7), the chamber was refilled with ultra-high purity (UHP) grade argon, and the temperature was raised to 900 °C to melt the sample and establish a homogeneous melt. The crucible was then translated downward at a rate of 1 mm/hr. The result of this first attempt is shown in Figure 9, right. We again observed the formation of black residue primarily at the top surface of the sample. The residue can be due to the chemical reduction of organic impurities in the starting materials and/or degradation of the glassy carbon crucible material. Our later experiments with LLF (Section III.a.v) indicate that the black residue is not due to the glassy carbon crucible. Furthermore, the sample consisted of several crystal domains rather than a single crystal. This could be due to an incorrect temperature gradient in the growth section, the presence of a dull tip in the crystal seed area, interference of eutectic material with the YLF growth, or a combination thereof.



**Figure 9:** Left: Type B Bridgman crucible cut to the correct length. Right: 5 g polycrystalline YLF:10%Yb sample obtained from the first Bridgman growth attempt.

A portion of the polycrystalline YLF:10%Yb sample was sent to Prof. Sheik-Bahae's laboratory for optical characterization. A 1040-nm laser was directed at the sample, and the sample temperature was observed using a thermal camera. It was found that the sample showed significant laser-induced heating, which can be a result of impurities present in the starting materials or introduced during sample preparation. We have recently sent polycrystalline samples of each of the starting materials to Prof. Sheik-Bahae to test if they show laser-induced heating, which would indicate the source of the impurities.

#### **iv. Growth of LLF**

The second material currently being grown is undoped LLF. We have procured a Czochralski-grown boule of undoped LLF (~85 g) from AC Materials Inc. which we are using as starting material. A crystallographically-oriented optical-quality sample was prepared from this boule and was sent to MARBLE team of Prof. Sheik-Bahae who measured a background absorption coefficient of  $\alpha_b = 3.3 \times 10^{-4} \text{ cm}^{-1}$ . While previous record laser-cooling samples showed  $\alpha_b < 10^{-4} \text{ cm}^{-1}$ , this is a relatively low value and makes this LLF boule a good starting material for the growth of RBL crystals.



**Figure 10:** 4.1 g sample of LLF obtained from melting crystalline LLF starting material in a Type B Bridgman crucible in the glovebox.

In contrast to YLF, LLF melts congruently (Figure 8, right), *i.e.* the crystal and melt composition remain identical when starting from a  $\text{YF}_3\text{:LiF}=0.50\text{:}0.50$  stoichiometry. This eliminates potential interference by eutectic material during the crystal growth, and it theoretically allows for 100% yield. In a first step, we melted several pieces from the LLF boule (4.1 g total) in a Type B Bridgman crucible in the glovebox. This involved heating the starting material at 10 K/min to 900 °C, dwelling for 2 hours, and then letting the furnace self-cool. The sample obtained from this melting step is shown in Figure 10. The absence of black residue is immediately apparent. We can thus conclude that the black residue observed in the YLF:Yb growth are not due to the crucible but rather inherent to the starting materials. We suspect that at least one of the YLF:Yb



starting materials contains organic impurities that then chemically reduce to elemental carbon (visible black residue) at the high temperature in the oxygen-free argon atmosphere. A possible remedy may be to wash the starting powders in an organic solvent (*e.g.* acetone or methanol) in order to dissolve organic residues on the surfaces prior to using the material for growth. The LLF starting material did not suffer this issue as it already went through a crystal growth that may have removed these impurities. In fact, it is a common observation in the Czochralski growth of fluorides that a film of (unknown) residues initially forms on the melt surface, and this film is routinely removed by scooping it up with a platinum mesh prior to growth. It is possible that this film of residue is also due to reduced organic impurities. Furthermore, we note in Figure 10, that the LLF sample has a generally more crystalline morphology compared to the highly polycrystalline YLF:Yb. This could be due to the absence of black residue as well as the absence of eutectic material interfering with the crystallization process. We are in the process of performing a Bridgman growth with this LLF sample.

**b. Theory and Modeling**

None.

**c. Analysis, Conclusions, Difficulties Encountered**

We have successfully performed the required modifications to the existing  $\mu$ PD system and are now in a position to develop the growth of RBL crystals using the Bridgman technique. We performed mass spectroscopy of the atmosphere in the growth chamber during pumping and concluded that hydrogen is at a sufficiently low level to not cause substantial reduction of  $\text{Yb}^{3+}$  to  $\text{Yb}^{2+}$ . It should therefore be possible to grow RBL crystals low in  $\text{Yb}^{2+}$  without using undesired reactive growth atmospheres. First samples of YLF:Yb and LLF were prepared. The presence of black residue in the YLF:Yb sample and the absence of that residue in the LLF sample led us to conclude that the commercial YLF:Yb starting materials contain organic impurities. It is thus not surprising that the YLF:Yb sample did not show net laser cooling. Furthermore, we observed a much higher degree of crystallinity in a sample of LLF compared to YLF:Yb, indicating that a congruently melting material is favorable for Bridgman growth.

The hiring of a student was delayed because of an initial lack of qualified candidates. The challenge was to identify a candidate who is willing to work at both UNM and LANL (separated by 100 miles) and who is eligible to be granted access to a controlled laboratory at LANL. This has significantly limited the rate of progress as all work reported here has been performed by the co-PI himself. We have since been successful in hiring Dr. Azzurra Volpi from the University of Pisa as a Postdoctoral Researcher to have a joint appointment in both Dr. Hehlen's and Prof. Sheik-Bahae's groups. Dr. Volpi has arrived in September 2017 and brings extensive experience in both the crystal growth and characterization of fluoride laser-cooling materials. She plans to split her time equally between UNM and LANL, which will greatly enhance our rate of progress in the second project year.





#### **IV. Collaborations/Synergy with other MARBLE Team(s) (*or other institutions*)**

We have close collaborations with the MARBLE Teams of Prof. Sheik-Bahae and Prof. Mafi. This includes a bi-weekly project meeting at UNM. Prof. Sheik-Bahae's team has performed first optical characterizations of a YLF:Yb sample grown at LANL, and measurements on the respective individual starting materials are underway. We have also delivered several YAG:Yb and ZBLAN:Yb samples to Prof. Sheik-Bahae's and Prof. Mafi's teams. These samples were from an existing collection of laser-cooling materials at LANL, and they have allowed the UNM teams to begin the development the optical experiments while more materials are being ordered.

We are also collaborating with the MARBLE team of Prof. Pauzauskie at the University of Washington. We have sent them a first sample of YLF:Yb, and Prof. Pauzauskie's students are currently performing EXAFS measurements on it.

Finally, we have regular correspondence with Prof. Tonelli (University of Pisa, Italy) and Dr. Krämer (University of Bern, Switzerland). The collaboration with Prof. Tonelli on  $\mu$ PD crystal growth goes back several years, and his advice on modifying the system has been very valuable. Dr. Krämer is an expert in the synthesis and properties of halide single crystals, and I have collaborated with him loosely for 25+ years. He has provided valuable insights on crucible materials, melt wetting, and  $\text{Yb}^{2+}$  formation. I will visit Dr. Krämer at the University of Bern in November 2017 as part of a different trip to Switzerland.

#### **V. Planned Year-2 Activities**

We will continue the development of the Bridgman crystal growth and begin experimentation with purified precursors. Candidate purification processes include the chemical purification using solvent extraction or ion exchange of precursor solutions and the electrochemical purification of the fluoride melt. Success of these methods will be gauged by measurements of external quantum efficiency and background absorption coefficient. With a growth process established, we will grow  $\text{Er}^{3+}$  and  $\text{Tm}^{3+}$  doped crystals as well as  $\text{Yb}^{3+}$ ,  $\text{Tm}^{3+}$  co-doped crystals for the subsequent study of two-tone RBL schemes.

The development of doped chalcogenide glasses will be advanced in parallel, with the ambitious goal of having a material system downselected and a preform extrusion system operational by the end of the second project year.

#### **VI. Personnel Supported in Year-1 (*names, titles*)**

Dr. Markus Hehlen, co-PI (LANL, NMC, UNM)

Dr. Azzurra Volpi, Postdoctoral Researcher (UNM), started in September 2017.



**VII. Publications** (*journal, conference, dissertations, ...*)

None.